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MA X B, ZHAO Z J, HAN L W, et al. Remediation effects of biochar on cadmium-contaminated soils with humic acid[J]. *Journal of Agro-Environment Science*, 2023, 42(1): 55–64.



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腐植酸作用下生物炭对Cd污染土壤的修复效果

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摘要: 为了探讨腐植酸对生物炭修复重金属污染土壤的影响, 通过土培试验, 分析两种不同添加量(0.1%和1%, *m/m*)的腐植酸[胡敏酸(HA)、富里酸(FA)]与两种生物炭[玉米秸秆生物炭(CBC)、稻壳生物炭(RBC)]复配处理下污染土壤中Cd形态的变化, 并探究不同腐植酸作用下生物炭稳定Cd的差异和机制。结果表明: 腐植酸增强了生物炭对土壤中Cd的稳定化程度。与未处理组相比, 1% HA和1% FA作用下的CBC使土壤中残渣态Cd占比升高了145.89%和117.96%, RBC使残渣态Cd占比升高了124.04%和159.58%。1%腐植酸添加量处理显著降低了土壤pH, 提高了土壤阳离子交换量(CEC)、土壤有机质(SOM)和有效磷含量。生物炭表面具有丰富的含氧官能团、芳香碳, 其可通过静电吸引、络合、表面沉淀和阳离子- π 键相互作用等结合重金属离子。综合来看, 1% FA和RBC复配添加对Cd污染土壤的修复效果最佳, 其使污染土壤的CEC、SOM和有效磷含量上升了24.56%、27.14%和34.81%, 并且使重金属Cd迁移指数下降了65.85%。

关键词: 重金属污染; Cd; 生物炭; 腐植酸; 修复效果

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Remediation effects of biochar on cadmium-contaminated soils with humic acid

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Abstract: To investigate the effects of humic acid on biochar remediation of heavy metal-contaminated soils and the morphological changes of Cd in contaminated soils, two different humic acid[humic acid(HA) and fulvic acid(FA)](0.1% and 1%, *m/m*) and two kinds of biochar[corn straw biochar(CBC) and rice husk biochar(RBC)] were evaluated via soil culture experiments. Twelve kinds of soil amendments were prepared in soil culture experiments to reveal the differences and mechanisms of biochar stabilization of Cd under different humic acids. The results of the present study were as follow: Humic acid enhanced the stabilization of Cd in soil by biochar. Compared with the untreated group, the percentage of residual Cd in the soil increased by 145.89% and 117.96% with CBC under the action of HA (1%) and FA (1%) and 124.04% and 159.58% with RBC under the action of HA (1%) and FA (1%), respectively. High humic acid addition(1%) significantly reduced soil pH and increased the cation exchange capacity(CEC), soil organic matter(SOM), and

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available phosphorus content of the soil. The surface of biochar was rich in oxygen-containing functional groups and abundant aromatic carbon, which can bind heavy metal ions through complexation, surface precipitation, and cation- π -bond interactions. In summary, the combination of 1% FA and RBC have the best remediation effect on Cd-contaminated soils. The co-application of FA and RBC increase the CEC, SOM, and available phosphorus content of the contaminated soil by 24.56%, 27.14%, and 34.81%, respectively and decrease the Cd migration index by 65.85%.

Keywords: heavy metal pollution; cadmium; biochar; humic acid; remediation effect

矿山开采以及化肥、农药的大量使用加剧了我国农田土壤重金属Cd的污染程度^[1],并因此衍生出土壤板结、盐渍化、土壤微生物生境破坏、人体健康风险等问题^[2]。土壤中重金属污染的修复方法主要有客土法、溶液淋洗、电动修复、植物修复和化学稳定法等^[3]。化学稳定法是通过施加修复剂来降低土壤中重金属的迁移性和生物有效性,从而达到修复重金属污染土壤的目的^[4]。

生物炭呈碱性,孔隙结构发达、比表面积大、活性官能团丰富,其可通过自身特性及对土壤理化性质的改变影响重金属的形态。生物炭所含的碱性物质可促进不溶性重金属的氢氧化物、碳酸盐和硅酸盐的形成,从而降低有效态重金属含量^[5];其表面含氧官能团、 CO_3^{2-} 及 PO_4^{3-} 可促进土壤中的重金属向有机结合态和残渣态转化^[6-7];此外生物炭可通过提高土壤pH增强黏土矿物、水合氧化物和有机质对重金属的吸附作用^[8-9],或通过改变土壤微生物结构和酶活性影响重金属形态^[10]。因此,生物炭被广泛应用于重金属污染土壤的修复^[11-15]。

在实际修复应用中,复合类修复剂的修复效果常好于单一修复剂^[16-17],如生物炭和腐植酸复配施用^[18]。腐植酸作为土壤中重要的有机成分,其含量和类型对土壤中重金属的迁移具有显著影响^[19-20]。胡敏酸和

富里酸是腐植酸中活性较高的两种成分,含有丰富的羧基、羟基、羰基等官能团,可通过吸附、氧化还原和络合等作用固定重金属^[21-24]。在腐植酸作用下,生物炭可使土壤中的Cd活性降低,油菜对Cd的积累量也因此减少^[18]。腐植酸与生物炭复配作用的效果受多种因素影响,成分来源、添加量、添加比例的不同均会使土壤修复效果产生差异^[25-26]。因此,两种成分腐植酸在不同添加量下对生物炭稳定土壤中重金属Cd的影响有待进一步研究。

基于此,本文拟通过土培试验,讨论腐植酸与生物炭复配对Cd污染土壤理化性质的影响,探究腐植酸对生物炭稳定污染土壤中Cd的作用效果及机理,以为Cd污染土壤修复工作提供理论参考。

1 材料与方法

1.1 供试材料

本试验所用两种生物炭分别由玉米秸秆粉末与稻壳粉末在缺氧条件下缓慢升温至500℃后热解2h制得。腐植酸购买自西亚化学股份有限公司。供试土壤采自甘肃省白银市东大沟中游一处农田表层(0~20 cm),场地坐标为104°16'31"E,36°29'37"N。土壤理化性质和重金属含量如表1所示。

供试材料的有机元素含量如表2所示。

表1 供试土壤的基本理化性质
Table 1 Physico-chemical properties of the tested soils

pH	电导率 Electrical conductance/ $(\mu\text{S}\cdot\text{cm}^{-1})$	有机质 Soil organic matter/ $(\text{g}\cdot\text{kg}^{-1})$	阳离子交换量 Cation exchange capacity/ $(\text{cmol}\cdot\text{kg}^{-1})$	总Cd含量 Total Cd content/ $(\text{mg}\cdot\text{kg}^{-1})$
8.21±0.05	172.9±16.3	7.57±1.46	3.55±0.32	31.12±1.22

表2 实验材料有机元素分析
Table 2 Analysis of organic elements in experimental materials

材料 Sample	元素质量占比 Elemental mass ratio/%					原子比 Atomic ratio	
	C	H	O	N	S	C/H	O/C
胡敏酸 HA	56.01	3.17	39.17	1.07	0.58	1.47	0.52
富里酸 FA	38.32	5.25	46.56	5.89	3.98	0.61	0.91
玉米秸秆生物炭 CBC	65.68	2.09	30.97	1.19	0.07	2.62	0.35
稻壳生物炭 RBC	34.70	0.75	63.98	0.44	0.14	3.86	1.38

1.2 试验设计

土培试验选择两种不同的生物炭,即玉米秸秆生物炭(CBC)和稻壳生物炭(RBC),分别配比高质量分数(1%,H)和低质量分数(0.1%,L)的胡敏酸(HA)、富里酸(FA),材料混合后均匀添加在受试土壤中进行60 d的培养。为防止土壤样品及重金属淋溶流失,将聚乙烯容器底部用保鲜膜密封。试验共设置13个处理:T0(CK),T1(CBC),T2(RBC),T3(HA_H),T4(FA_H),T5(CBC+HA_L),T6(CBC+HA_H),T7(CBC+FA_L),T8(CBC+FA_H),T9(RBC+HA_L),T10(RBC+HA_H),T11(RBC+FA_L),T12(RBC+FA_H),每组设置3个平行。为保持良好的水力条件以促进修复剂对重金属的稳定作用,土壤含水量保持为最大田间持水量的70%,3 d补充1次水分。培养过程中,分别采集第10、20、30、60天的土壤,土样自然风干研磨,并分别过2 mm和0.15 mm尼龙筛后保存于密封袋中,用于土壤pH和重金属形态含量分析,另外测定培养60 d后土壤的有机质(SOM)含量、土壤阳离子交换量(CEC)、有效磷含量。

材料表征:将生物炭与腐植酸混合均匀后分层埋入受试土壤中以探究材料在土壤修复前后的表面性质变化。保持与土培试验相同的条件,在受试土壤中进行60 d无扰动培养后,提取出混合材料,将其冷冻干燥后进行表征分析。

1.3 分析测定方法

土壤pH采用pH计测定,水土比为2.5:1(V/m)^[27];CEC、SOM含量、有效磷含量和Cd形态分布分别采用乙酸钙法^[28]、重铬酸钾外加热法^[29]、联合浸提比色法^[30]和改进BCR顺序提取法^[31]测定。

重金属迁移指数(M)是一种指示重金属稳定化程度的指标^[32-33],M值越小,表明重金属在环境介质中的稳定性越好。

$$M = -\Delta_{\text{res}} - 0.33\Delta_{\text{oxid}} + 0.33\Delta_{\text{redu}} + \Delta_{\text{acid}}$$

式中: Δ_{res} 为残渣态Cd占比; Δ_{oxid} 为可氧化态Cd占比; Δ_{redu} 为可还原态Cd占比; Δ_{acid} 为弱酸提取态Cd占比。

1.4 材料表征方法

使用傅里叶红外光谱仪(NEXUS 670)和光电子能谱仪(岛津 Axis Supra)分析腐植酸与生物炭材料在污染土壤中培养前后的表面官能团、表面元素及价态变化,使用有机元素分析仪(Elementar vario EL cube)分析材料中的有机元素含量。

1.5 数据统计分析

利用Excel 2016和Origin 2018进行数据分析和制图,利用SPSS 22进行统计分析,单因素ANOVA法

进行显著性检验, $P < 0.05$ 表示处理间差异显著。

2 结果与讨论

2.1 生物炭、腐植酸单独及复配对土壤理化性质的影响

不同修复剂对土壤pH的影响如图1所示。供试土壤pH随培养时间延长均呈下降趋势,经60 d土壤培养后,与CK相比,生物炭和腐植酸的添加改变了土壤pH。CBC和RBC的加入使土壤pH升高了0.2~0.3个单位。HA使土壤pH下降了0.23个单位。1% FA的添加显著改变了土壤的pH,使之下降了0.6~1.0个单位,pH最低达到了7.2(T12)。在复配条件下,生物炭与腐植酸降低了土壤pH,且高腐植酸含量处理更明显。生物炭由于其芳香共轭结构和富含碳酸盐的灰分而呈碱性,其加入土壤后会提高土壤的pH,但由于污染土壤本身pH较高,是典型的碱性土壤,因此石灰效应不显著^[27]。HA在中性或者弱碱性土壤中会有少量溶解,其含有的酸性基团可以使土壤pH降低。FA是在酸碱条件下都可溶解的小分子腐植酸,研究表明,FA的添加可以增加体系中的 H^+ 浓度,从而对土壤pH产生影响^[34]。

CEC是土壤缓冲能力的评价指标,是评估土壤保肥能力和土壤改良的重要依据。不同材料添加60 d后对土壤CEC的影响如图2所示。各材料均能有效提高土壤CEC。在土壤中单独添加CBC和RBC使土壤CEC分别从 $3.39 \text{ cmol} \cdot \text{kg}^{-1}$ 提升至 $3.79 \text{ cmol} \cdot \text{kg}^{-1}$ 和 $3.92 \text{ cmol} \cdot \text{kg}^{-1}$;FA以及FA与生物炭的复配使土壤CEC上升了3.92%~24.29%;HA的添加则显著提高了土壤中CEC,单独添加HA以及HA与CBC和RBC复配添加使土壤CEC上升了53.39%~87.91%。1% FA

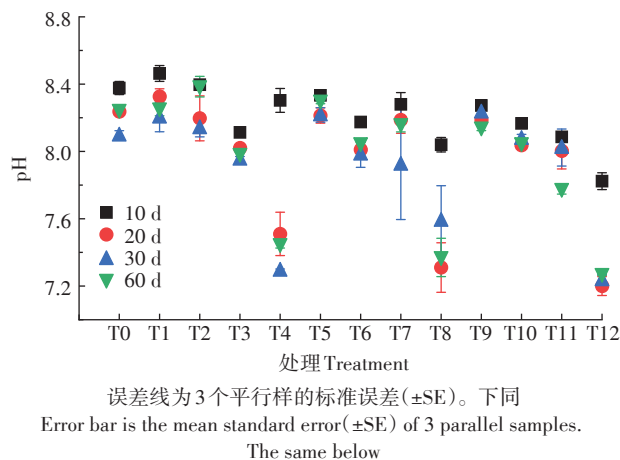
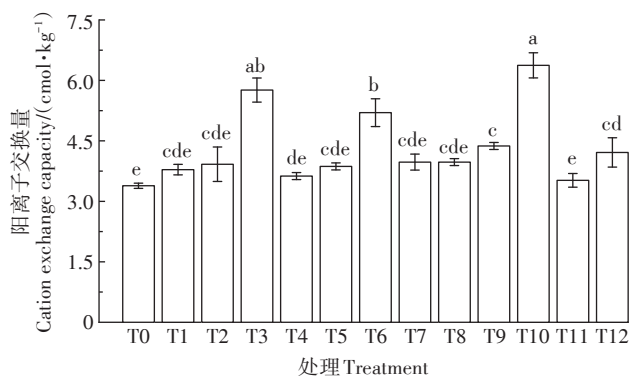


图1 不同材料对土壤pH的影响

Figure 1 Effects of different materials on soil pH

和RBC复配添加使土壤CEC上升了24.56%。相较而言,HA对土壤CEC提高效果更明显。生物炭和腐植酸的官能团丰富,并且各种氧化作用也增加了生物炭表面的官能团,因此其有较强的阳离子吸附能力,可使土壤CEC上升^[35-36]。结果表明,土壤缓冲能力在添加各种材料后得以增强,尤其生物炭与腐植酸复配作用更显著。



不同小写字母表示处理间差异显著($P<0.05$)。下同
Different lowercase letters indicate significant differences among treatments($P<0.05$). The same below

图2 不同材料添加60 d后对土壤CEC的影响

Figure 2 Effects of different materials on soil CEC after 60 days

SOM可以改良土壤结构、提高土壤持水能力,其含量升高有助于提高土壤重金属的稳定性^[37]。图3为不同材料添加60 d后对SOM含量的影响。单独添加生物炭以及生物炭与低腐植酸复配添加对SOM作用不显著,其含量变化为-5.47%~10.87%;单独施加HA以及1% HA与生物炭复配使SOM含量提高了21.74%~81.52%,FA以及1% FA与生物炭复配使SOM含量提高了10.84%~27.14%。相较而言,1% HA与生物炭复配作用对SOM含量的影响更大。

土壤中的有效磷含量是作物生长发育的关键条件之一,它影响着土壤重金属形态分布,是评价土壤质量的重要指标^[38]。由图4可知,60 d后,CBC和RBC单独作用下土壤有效磷含量仅提高了8.1%和6.3%。HA与生物炭复配添加使土壤有效磷含量上升了10.26%~37.58%,FA与生物炭复配添加使土壤有效磷含量上升了14.53%~34.81%。腐植酸对土壤中钙、铁、锰、铝等离子的亲和力强,因此可以通过结合土壤中钙、铁、锰、铝等离子,抑制土壤对磷的固定,提高土壤中磷的有效性。总体上看,HA和FA的加入均提高了土壤中的有效磷含量。

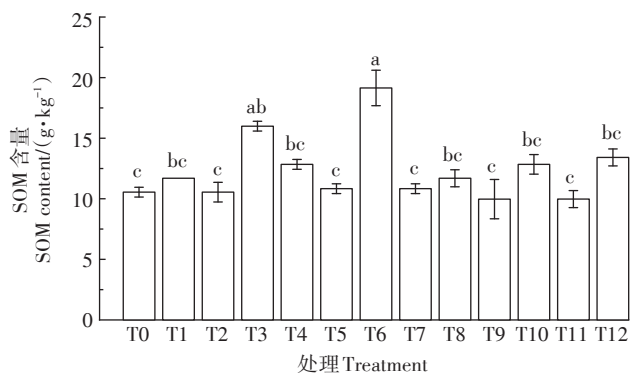


图3 不同材料添加60 d后对SOM的影响

Figure 3 Effects of different materials on SOM after 60 days

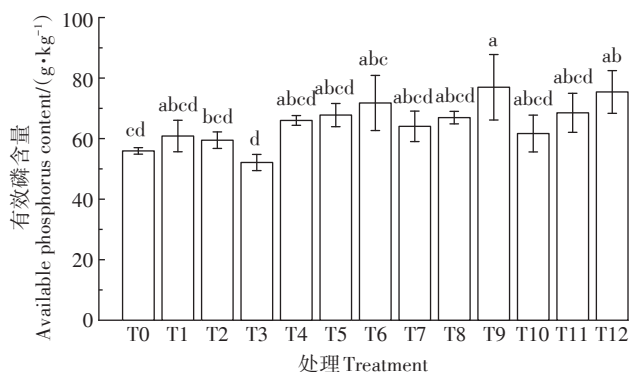


图4 不同材料添加60 d后对土壤有效磷含量的影响

Figure 4 Effects of different materials on the content of available phosphorus in soil after 60 days

2.2 生物炭、腐植酸单独及复配对污染土壤中Cd的稳定效果

2.2.1 对污染土壤中Cd形态变化的影响

重金属赋存形态决定其环境行为和生物有效性,直接影响重金属的迁移和循环。改进BCR连续提取法可以将土壤中的Cd分为弱酸提取态、可还原态、可氧化态和残渣态4种。弱酸提取态具有较高的活性和毒性,而可还原态、可氧化态和残渣态的危害相对较小^[39]。本试验原状土壤中Cd主要以弱酸提取态存在,各形态占比大小依次为弱酸提取态>可还原态>残渣态>可氧化态。

施用生物炭与腐植酸后,土壤不同时间Cd形态分布如图5所示。在不同修复剂作用下,10 d时土壤中弱酸提取态Cd占比降低了12.70%~25.40%,弱酸提取态Cd占比降低最多的为T10处理。20 d时弱酸提取态Cd占比降低了15.87%~26.98%;残渣态Cd占比相比于CK升高了1.07~1.73倍,同时可还原态Cd占比降低了15.78%~57.89%。30 d和60 d时的土壤

弱酸提取态Cd占比与前20 d变化趋势一致,没有显著改变,说明腐植酸与生物炭复配应用于此污染土壤中,在20 d时稳定土壤重金属Cd的程度最高,并在短时间内变化较小。

0.1%腐植酸处理60 d后(T5、T7、T9和T11),土壤中Cd各个形态含量占比发生变化,主要表现为弱酸提取态向可还原态和残渣态的转化。不同腐植酸复配生物炭作用下,弱酸提取态Cd占比降低了18.32%~26.13%,残渣态Cd占比增加了0.91~1.52倍。1%腐植酸处理(T6、T8、T10和T12)后,弱酸提取态Cd占比降低了21.19%~28.84%,残渣态Cd占比增加了1.18~1.60倍。1% HA和1% FA作用下的CBC使土壤中残渣态Cd占比升高了145.89%、117.96%,RBC使残渣态Cd占比升高了124.04%、159.58%。

由此可知,单独施加腐植酸或生物炭时污染土壤中弱酸提取态重金属的减少量明显低于生物炭与腐植酸复配添加,尤其对比0.1%和1%腐植酸对Cd化学形态转化的结果发现,1%腐植酸能使更多活性较高的弱酸提取态Cd转化为稳定的残渣态Cd。

2.2.2 对污染土壤中Cd迁移能力的影响

生物炭、腐植酸单独及复配作用下土壤Cd的迁移指数随时间的变化情况如图6所示。由图6可知,CBC单独添加60 d后使土壤Cd迁移指数从0.41下降至0.24。1% HA与CBC复配以及1% FA与CBC复配分别使迁移指数下降至0.17和0.24。RBC单独添加使60 d后土壤Cd迁移指数从0.41下降至0.26。1% HA与RBC复配以及1% FA与RBC复配分别使土壤Cd迁移指数下降至0.19和0.14。可见,两种生物炭的添加都有效降低了土壤中Cd的迁移能力,并且随腐植酸添加量的上升迁移指数下降,即稳定效果提高。HA的加入有效促进了RBC在短期内稳定重金属的效果,尤其在20 d内,土壤Cd迁移指数下降相较于单一生物炭更快。0.1% HA以及FA都在20 d内促进了Cd的钝化并且在30 d后趋于稳定。值得注意的是,1%的腐植酸作用下生物炭在30 d后有进一步降低Cd迁移能力的趋势,说明1%添加量的腐植酸能够有效提高RBC对Cd的稳定能力。

生物炭、腐植酸单独及复配作用对污染土壤的修

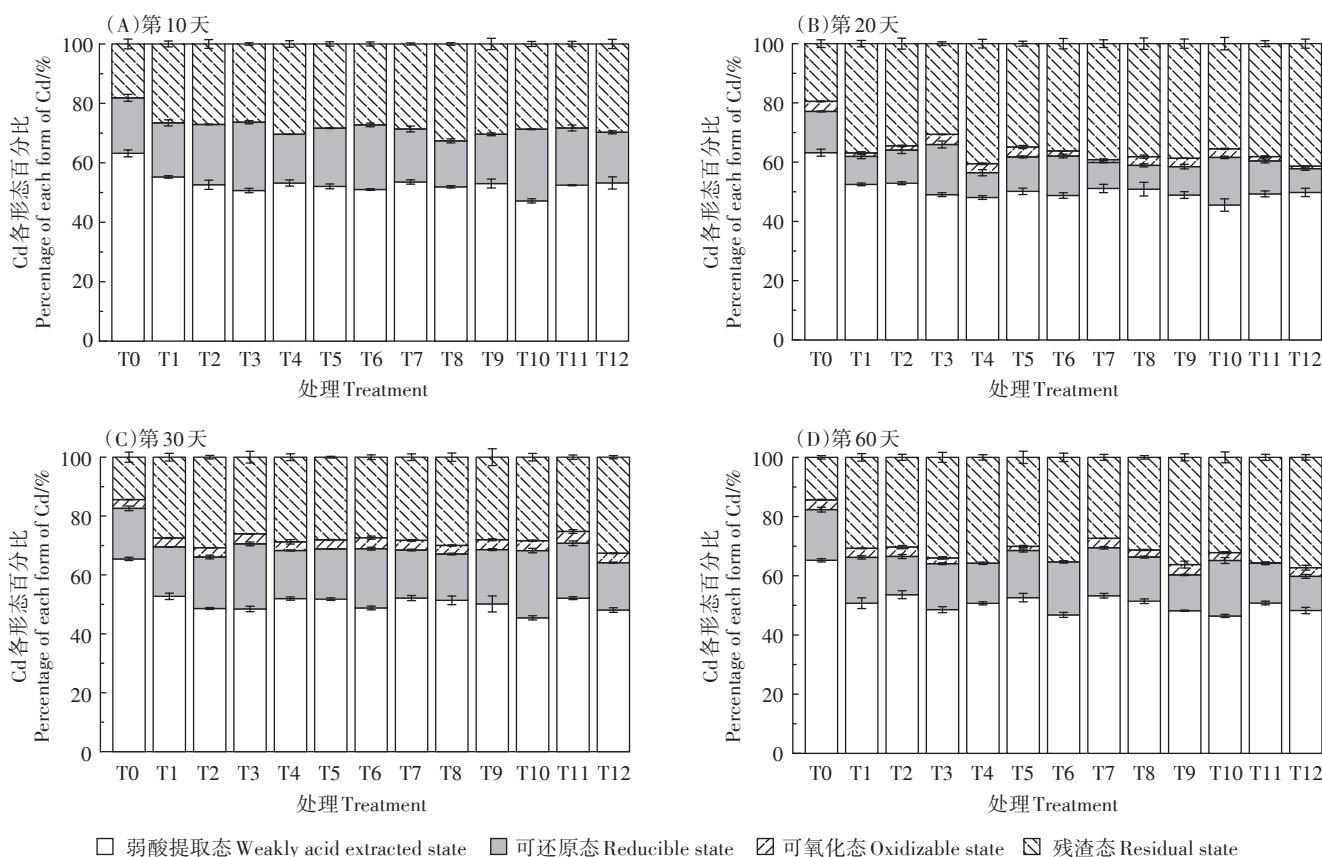


图5 不同处理组在第10、20、30、60天时Cd的形态变化

Figure 5 Morphological changes of Cd on the 10th, 20th, 30th and 60th day of different treatments

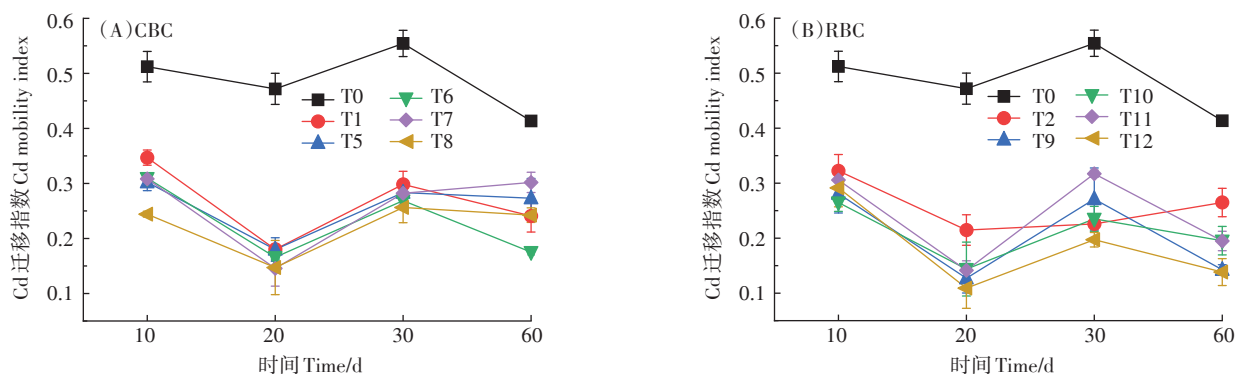


图6 不同材料对土壤Cd迁移指数的影响

Figure 6 Effects of different materials on soil Cd migration index

复效果高低为:FA复配RBC>HA复配CBC>HA复配RBC>FA复配CBC>CBC>RBC。其中1%FA复配RBC对Cd的迁移指数降低最多,下降了65.85%。

在添加材料处理中,生物炭与腐植酸复配材料对受试土壤中重金属Cd的稳定效果明显,这可能与两者共同作用提高了SOM、有效磷含量及CEC有关。HA、FA分别与生物炭复配作用使受试土壤中SOM含量上升了21.74%~81.52%和10.84%~27.14%。生物炭和腐植酸富含有机碳,其不仅可以直接提高SOM含量,还可通过促进土壤团聚体的形成和稳定来间接提高SOM含量^[40-41],而SOM又可与重金属离子形成络合物,从而降低重金属活性^[42]。在腐植酸作用下,生物炭复配材料(T9、T12)使土壤有效磷含量显著升高($P<0.05$),从而降低了重金属活性。腐植酸可通过释放出土壤固定的磷来增加磷的有效性^[43-44],生物炭表面有Ca、Mg、P等多种矿物质,其中的 Ca^{2+} 、 Mg^{2+} 等阳离子可以与 Cd^{2+} 进行离子交换,而 CO_3^{2-} 、 OH^- 、 PO_4^{3-} 等阴离子又可与 Cd^{2+} 形成难溶性沉淀,从而降低Cd的有效性^[8,45]。相较于生物炭材料的单独添加,生物炭与腐植酸复配显著提高了土壤CEC(图2),增加了土壤可变负电荷,从而提高了土壤胶体对带正电荷重金属离子的静电吸引能力^[46]。

因此,腐植酸作用下的生物炭材料可通过改变土壤理化性质而显著影响Cd的稳定化程度。生物炭与腐植酸复配材料提高了SOM含量,降低了土壤Cd的活性,土壤有效磷含量的增加促进了 Cd^{2+} 形成磷酸盐沉淀,CEC提高则增强了土壤对Cd的吸附能力。

2.3 生物炭与腐植酸复配对Cd的稳定化作用机理

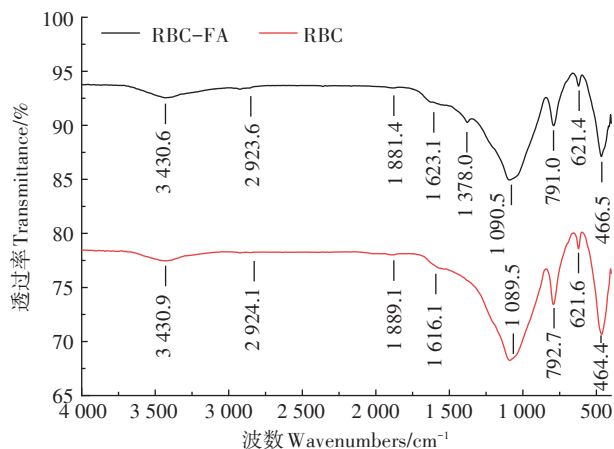
生物炭可以通过离子交换和表面沉淀的方式固定土壤中的Cd^[47-48],其表面的含氧官能团和芳香碳结构可通过表面络合和阳离子- π 键的方式稳定重金属

Cd^[49-51]。腐植酸(HA、FA)的添加,可促进生物炭对重金属Cd的稳定。为了探究生物炭与腐植酸复配作用对土壤Cd的稳定化机理,通过FTIR和XPS表征手段,研究复配材料添加到污染土壤中培养前、后的表面官能团变化。

有机材料的C/H、O/C可反映其芳香化程度和含氧官能团的多寡^[52]。从表2可知,CBC和RBC的C/H分别为2.62和3.86,说明RBC的芳香化程度高于CBC。HA、FA、CBC和RBC的O/C分别为0.52、0.91、0.35和1.38,其中RBC和FA的含氧官能团分别比CBC和HA高。因此,结合修复效果,本文选择1%FA复配RBC材料进行机理探究。

2.3.1 FA复配RBC材料在污染土壤中培养前后的FTIR分析

FTIR可以提供材料表面官能团的信息,图7为RBC在污染土壤中培养前后的FTIR图。由图7可知,RBC富含含氧官能团,如 $3\ 430.6\sim 3\ 430.9\text{ cm}^{-1}$ 处的宽吸收峰是—OH基团的伸缩振动^[53], $1\ 616.1\text{ cm}^{-1}$ 和 $1\ 623.1\text{ cm}^{-1}$ 处的吸收峰是—C=O基团的伸缩振动^[54]以及 $1\ 089.5\text{ cm}^{-1}$ 和 $1\ 090.5\text{ cm}^{-1}$ 处C—O基团的伸缩振动^[55]。RBC与FA复配下,RBC的表面官能团发生显著变化。 $1\ 378.0\text{ cm}^{-1}$ 处新出现的吸收峰为羧酸C—OH的伸缩振动,说明在土壤培养过程中RBC上一C=O基团和C—O基团的强度增加,即RBC同土壤中Cd的结合能力有所提高。 $2\ 924.1\text{ cm}^{-1}$ 和 $2\ 923.6\text{ cm}^{-1}$ 处的弱吸收峰是饱和C—H键的伸缩振动, 621.6 cm^{-1} 附近的峰是—OH的面外弯曲振动, 792.7 cm^{-1} 处的峰是芳香族C—H键的伸缩振动^[56]。 464.4 cm^{-1} 处为Si—O—Si键的反对称伸缩振动^[57]。综上所述,RBC表面具有丰富的含氧官能团和芳香C,并且与FA复配培养后,其表面官能团更有利于Cd



RBC:在土壤培养中培养前的RBC;RBC-FA:与FA复配在污染土壤中培养60 d后的RBC。下同

RBC:RBC before incubation in soil culture;RBC-FA:RBC incubation in contaminated soil in complex with FA after 60 days. The same below

图7 在污染土壤中培养前后的生物炭FTIR图像

Figure 7 FTIR images of biochar before and after incubation in contaminated soil

的结合。

2.3.2 FA复配RBC材料在污染土壤中培养前后的XPS分析

RBC的C1s和O1s精细谱图显示,其表面官能团在污染土壤中培养前后发生了显著变化(图8)。如图8C和图8D所示,284.6、285.5、286.7、288.3、293.4 eV和284.6、285.1、286.9、289.5、293.8 eV处的峰分别对应培养前后RBC的C=C/C—C、C—O、C=O、O—C=O和 π - π^* 基团。图8E和图8F所示为RBC稳定前后O1s的精细图谱,其中531.4、533.3、534.1 eV和531.6、533.1、534.5 eV处的峰对应C=O、O—C=O/O—OH、O—C=O/C—O基团^[58-59],该结果与FTIR获得的结果一致。即经过60 d土壤培养,RBC上289.5 eV对应的O—C=O峰高和半峰宽均增加,而293.8 eV对应的 π - π^* 基团峰高和半峰宽减小,这说明土壤中的氧化过程促进了羧基含量的增加且伴随着 π - π^* 基团的减少,这一过程可能会增强重金属离子同生物炭的结合^[60]。

综上所述可以看出RBC含氧官能团丰富,主要为C=O、O—C=O/O—OH、O—C=O/C—O基团。FA复配RBC在土壤中培养后其表面基团发生显著变化,RBC表面羧基基团含量增加,在1378.0 cm⁻¹处出现新的吸收峰。FA作用下RBC表面羧基基团的变化有利于其与重金属Cd的结合。

综上所述,在受试土壤中,腐植酸复配生物炭能

有效稳定重金属Cd,1% FA复配RBC使Cd的迁移指数下降了65.85%。在腐植酸作用下,生物炭修复Cd污染土壤的过程中SOM、有效磷含量和CEC升高,促进了Cd的稳定;FA复配RBC在土壤中培养后,RBC表面羧基官能团含量增加,有利于RBC同重金属的结合。因此,腐植酸(1% FA)复配RBC对污染土壤中Cd有较好的修复效果。

3 结论

(1)玉米秸秆生物炭(CBC)和稻壳生物炭(RBC)在受试土壤中均可降低Cd的迁移能力,提高其稳定性。胡敏酸(HA)和富里酸(FA)与生物炭复配可提高生物炭对Cd的稳定能力,但相较于CBC,FA和HA与RBC复配对土壤中Cd的稳定效果更好。1% FA和RBC复配添加对土壤中Cd的稳定效果最佳。

(2)在腐植酸作用下,生物炭材料可以显著改善污染土壤理化性质,从而促进Cd在土壤中的稳定化。其中FA复配生物炭材料可有效提高土壤中有效磷含量和阳离子交换量,降低土壤pH,HA与生物炭复配则对土壤中有机质含量有明显提升作用。

(3)RBC具有芳香C结构和丰富的含氧官能团,FA与RBC复配作用下RBC表面羧基官能团增加,有利于其与Cd的结合。

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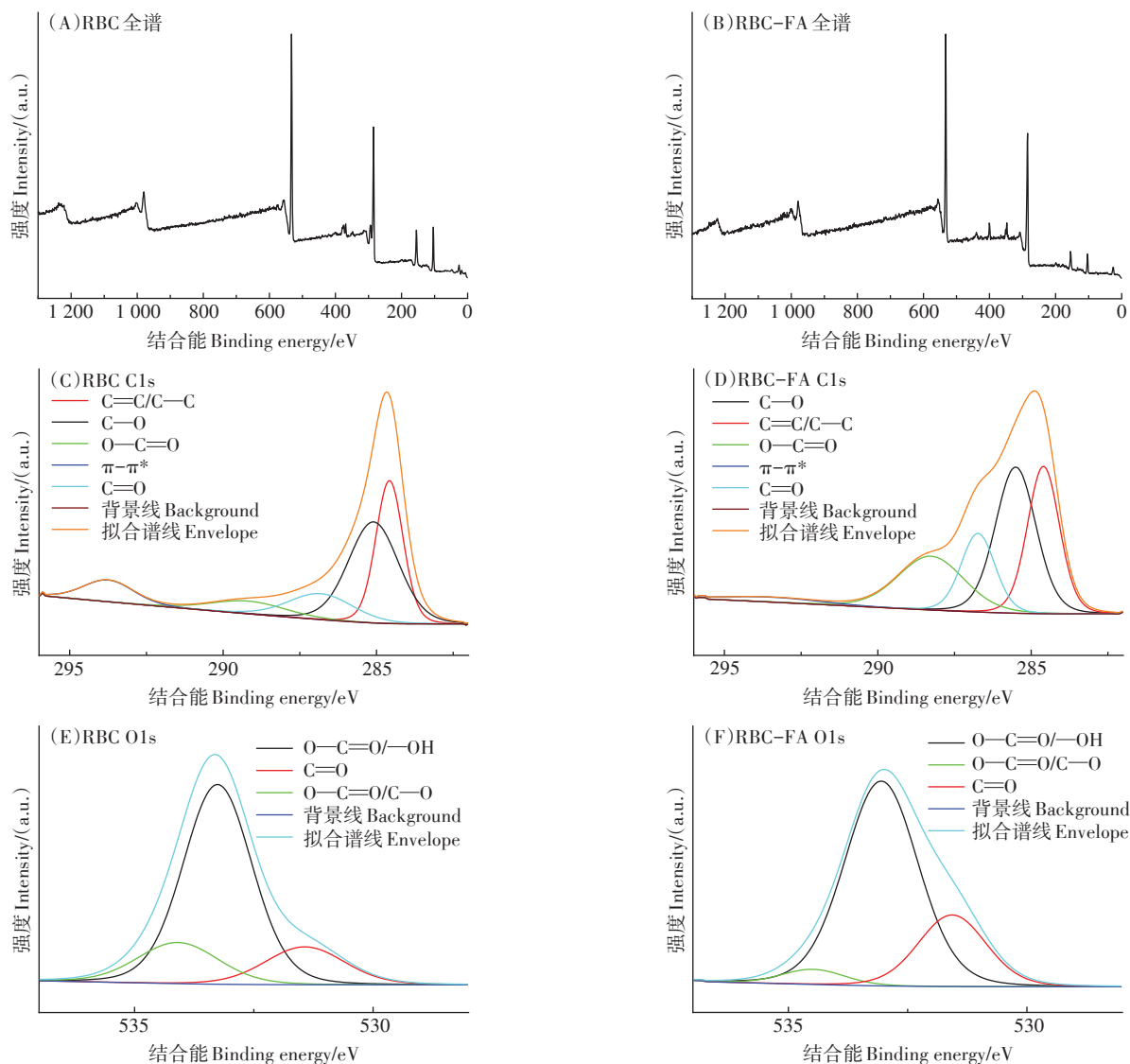


图8 在污染土壤中培养前后的生物炭XPS图像

Figure 8 XPS images of biochar before and after incubation in contaminated soils

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